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REPORT TITLE: Injection and Scattering of Polarized Spins at Nanoscale Polymer Interfaces

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Sincerely,

A handwritten signature in blue ink, appearing to read 'A. Epstein', with a long horizontal flourish extending to the right.

Arthur J. Epstein, PI  
The Ohio State University

<b>REPORT DOCUMENTATION PAGE</b>			Form Approved OMB NO. 0704-0188	
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1. AGENCY USE ONLY (Leave Blank)		2. REPORT DATE October 3, 2006		3. REPORT TYPE AND DATES COVERED Final Report, 1/1/02 to 5/31/04
4. TITLE AND SUBTITLE Injection and Scattering of Polarized Spins at Nanoscale Polymer Interfaces			5. FUNDING NUMBERS DAAD19-01-1-0562	
6. AUTHOR(S) Arthur J. Epstein				
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) The Ohio State University Department of Physics 191 W. Woodruff Avenue Columbus, OH 43210-1117			8. PERFORMING ORGANIZATION REPORT NUMBER	
9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES)  U. S. Army Research Office P.O. Box 12211 Research Triangle Park, NC 27709-2211			10. SPONSORING / MONITORING AGENCY REPORT NUMBER  4 2 4 4 2 . 7 - M S	
11. SUPPLEMENTARY NOTES The views, opinions and/or findings contained in this report are those of the author(s) and should not be construed as an official Department of the Army position, policy or decision, unless so designated by other documentation.				
12 a. DISTRIBUTION / AVAILABILITY STATEMENT  Approved for public release; distribution unlimited.			12 b. DISTRIBUTION CODE	
13. ABSTRACT (Maximum 200 words) We made excellent progress several directions. We demonstrated that V[TCNE] <sub>~2</sub> is a room temperature fully spin polarized magnetic semiconductor of interest for spintronic applications, including spin valves. We increased the coercivity (which is crucial for spintronics device) of the parent material V[TCNE] <sub>~2</sub> by doping with ions that have large magnetocrystalline anisotropy (Co, Fe, etc.). For Co and Fe substantially higher coercive fields, H <sub>C</sub> , than the pure V[TCNE] <sub>2</sub> (275 Oe for x = 0.3 and 1100 Oe for x = 0.05 at 5 K, respectively) were realized, while in case of Ni H <sub>C</sub> does not exceed 14 Oe. T <sub>C</sub> for the materials with x > 0.3 exceeds 300 K. We extended MR measurements to very high magnetic fields (up to 32 T) to observe the remarkable linear MR behavior below the ordering temperature predicted for this magnetic semiconductor. Ferrimagnetic resonance (FMR) studies have been performed on V[TCNE] <sub>~2</sub> using high frequency microwaves (240 GHz) to enhance the spectral resolution. Effective magnetization, M <sub>eff</sub> , intensity and linewidth behaviors of individual peaks indicate long-range magnetic ordering and also the presence of glassy nature due to the formation of multi-domains. XANES studies performed at ANL, show that vanadium ions are coordinated by 6 nitrogen atoms.				
14. SUBJECT TERMS spintronics, organic based magnetic semiconductor, magnetoresistance, spin polarized transport			15. NUMBER OF PAGES 5	
			16. PRICE CODE	
17. SECURITY CLASSIFICATION OR REPORT <b>UNCLASSIFIED</b>	18. SECURITY CLASSIFICATION ON THIS PAGE <b>UNCLASSIFIED</b>	19. SECURITY CLASSIFICATION OF ABSTRACT <b>UNCLASSIFIED</b>	20. LIMITATION OF ABSTRACT <b>UL</b>	

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**I. Statement of the Problem Studied**

We built on our discovery of a room temperature organic-based magnetic semiconductor to explore the opportunities for its use in spintronic devices. The results are very encouraging with better understanding of the structure, processing and magnetic properties. We also fabricated initial spintronic devices based on the organic magnetic semiconductor with initial success. In addition we have developed a new concept of spin nanogates.

**II. Summary of the Most Important Results**

We describe below how the composition of an organic based magnet can be controlled by varying the Chemical Vapor Deposition (CVD) conditions. A study was conducted for the  $\text{Co}_2(\text{CO})_8$  / TCNE system to form cobalt tetracyanoethylene  $[\text{Co}(\text{TCNE})_x, x \sim 2$ , a paramagnetic material], and for the  $\text{V}(\text{CO})_6$  / TCNE system to form vanadium tetracyanoethylene  $[\text{V}(\text{TCNE})_x, x \sim 2$ , a ferrimagnetic material]. Thin  $\text{V}(\text{TCNE})_2$  films ( $\sim 0.05$ - $0.5 \mu\text{m}$ ) with room temperature conductivity of  $10^{-4} < \sigma_{\text{RT}} < 10^{-3} \text{ S/cm}$  and magnetic ordering temperature  $T_c$  of up to  $\sim 400\text{K}$  were deposited. The  $\text{V}(\text{TCNE})_x$  thin films have the potential for incorporation in a spin valve device as one of the magnetic contacts, and also have the potential to form optically controlled magnetic-based (e.g., spin valve) structures.

Spintronic devices use the spin property of electrons in applications such as giant magnetoresistance-based magnetic read heads, spin valves, and spin light emitting diodes. The introduction of organic-based materials to replace conventional ceramics, metals or alloys offers some potential advantages: versatility of substrate materials (lower processing temperatures), control over the magnetic ordering temperature (by tailoring the composition), increased spin coherence lifetime through reduced spin-orbit and hyperfine couplings, and improved spin injection across interfaces. Of special interest is the material  $\text{V}(\text{TCNE})_2$ . Thick ( $\sim 5$ - $10 \mu\text{m}$ ) CVD made films are ferrimagnetic with an ordering temperature  $T_c$  of up to  $\sim 400\text{K}$ , and room temperature conductivity  $\sigma_{\text{RT}} \sim 10^{-4} \text{ S/cm}$ .

$\text{V}(\text{TCNE})_2$  films were deposited by CVD using vanadium hexacarbonyl  $[\text{V}(\text{CO})_6]$  and TCNE as source materials.  $\text{V}(\text{CO})_6$  was obtained via synthesis while TCNE is commercially available from Aldrich, and was used after purification. For the formation of  $\text{Co}(\text{TCNE})_2$  films we used  $\text{Co}_2(\text{CO})_8$  from STREM (also after purification). The CVD system is identical to the one described previously. These air sensitive films are handled in inert atmosphere throughout.

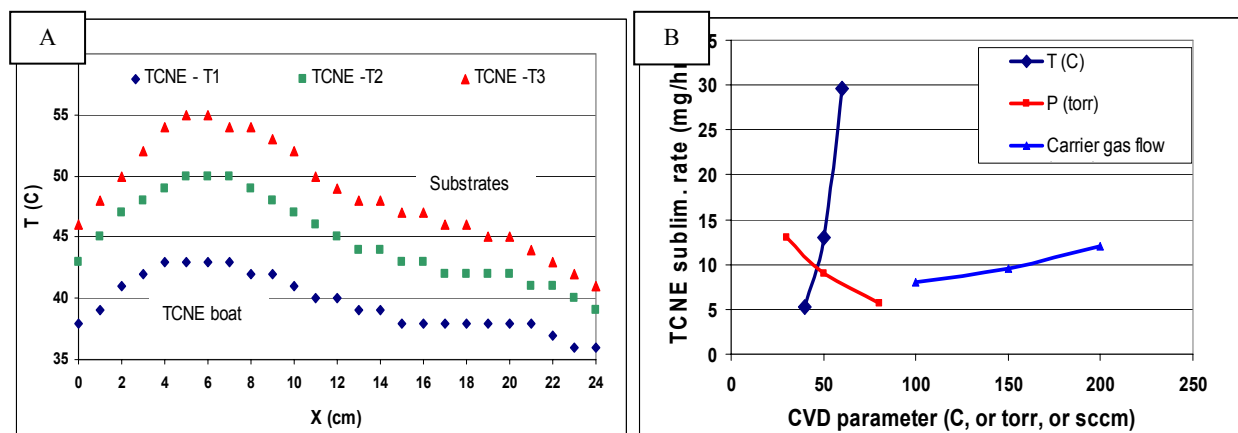
For resistance measurements, gold contacts of 100 nm thickness were deposited onto a glass substrate and  $0.5$ - $1 \mu\text{m}$   $\text{V}(\text{TCNE})_2$  films were deposited on top of these contacts over a gap. Spin valve devices were formed using cobalt as the first ferromagnet contact layer, and  $\text{V}(\text{TCNE})_2$  ( $0.1$ - $1 \mu\text{m}$ ) as the second one.  $\alpha$ -6T (sexithophene) was employed as a spacer which decouples the two ferromagnets. Contacts were made to both ferromagnets using aluminum or gold.

The transport behavior, and magnetoresistance response of the  $\text{V}(\text{TCNE})_2$  films were characterized using a Quantum Design Physical Property Measurement System (PPMS-9) by two point probe geometry. Samples were sealed in a sample holder after making electrical connection to the gold contact pads. Films

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show a resistance of about a  $M\Omega$  at room temperature. Photoinduced magnetic studies of  $V(TCNE)_2$  thin films on glass were performed on a SQUID magnetometer (Quantum Design).

To be able to control the formation of  $V(TCNE)_2$  and  $Co(TCNE)_2$  CVD films, we studied the process window of the precursors TCNE,  $V(CO)_6$ , and  $Co_2(CO)_8$  in our specific reactor geometry. Figure 1A presents temperature profiles along the reactor. There are two temperature zones created by different density of wrapping of the heating coil on the external heated sleeve. This geometry was created so that TCNE sublimation rate can be controlled separately from sample temperature. Figure 1(B) shows examples of our results for study of the TCNE sublimation rate (mg/hr) as a function of variation of temperature, pressure or Ar carrier gas flow (with the other two variables held constant). It can be seen that sublimation rate is most sensitive to temperature changes, followed by pressure, and finally by Ar carrier gas flow.



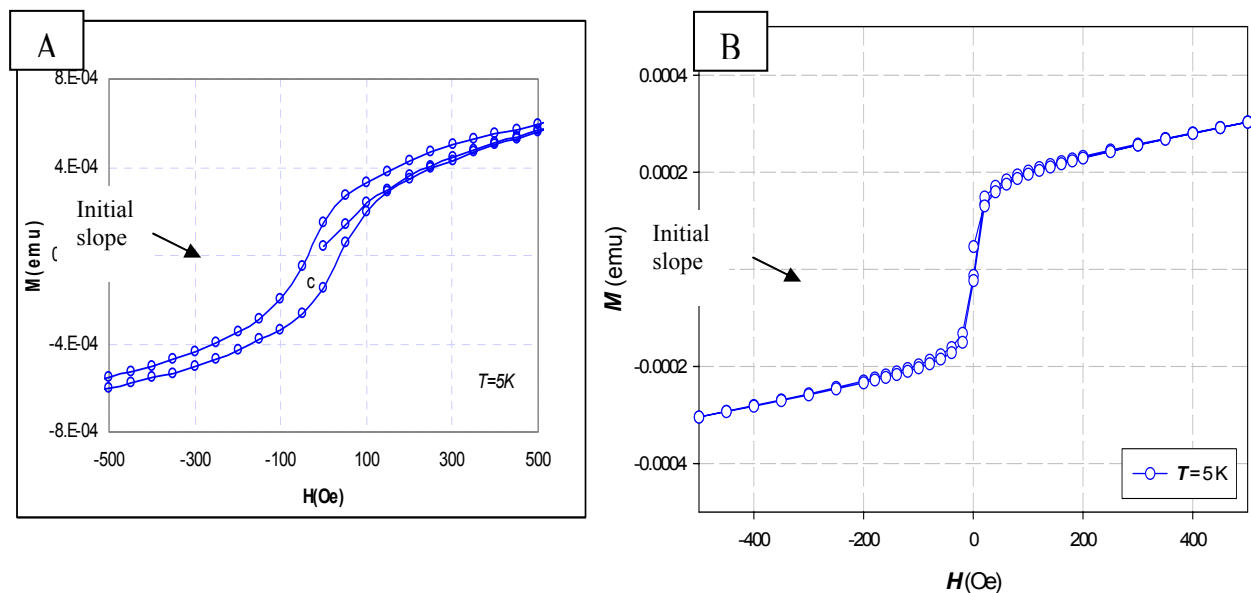
**Figure 1.** A) Temperature profiles along the CVD reactor, for three TCNE temperature settings B) dependence of TCNE sublimation rate on process parameters such as temperature, pressure, and carrier gas flow.

The reactions to produce  $V(TCNE)_2$  and  $Co(TCNE)_2$  respectively are:



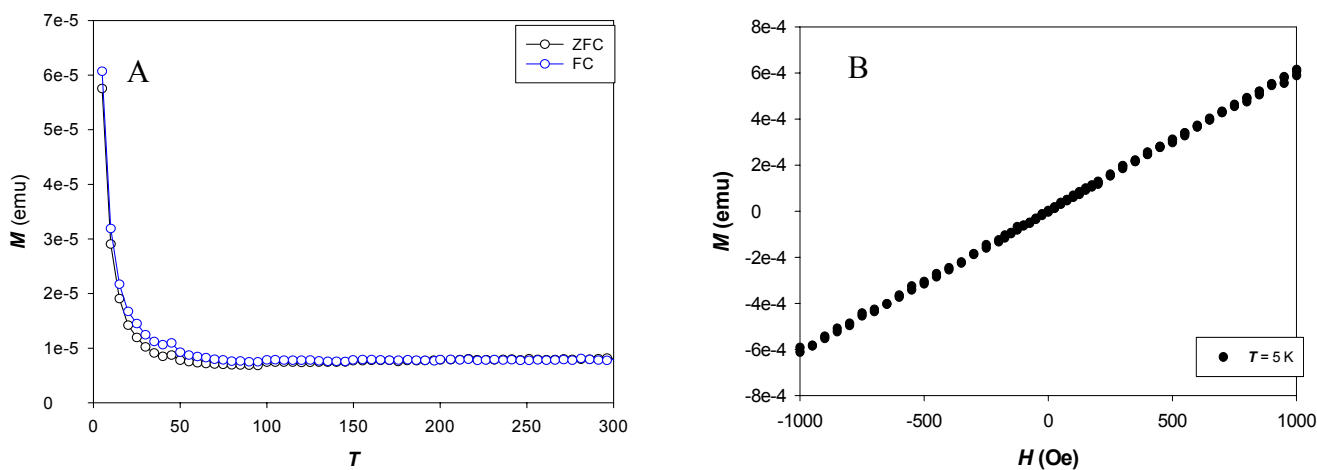
The metal carbonyl precursors, which are located in a 'T'-shaped boat outside the heated zone, are very volatile. Therefore, they are cooled to  $\sim 10^\circ C$ , and their sublimation rate is controlled by carrier gas flow, based on molar ratios between TCNE and metal carbonyl, and taking into account their molecular weights. The effect of this ratio is manifested in the magnetic properties of the formed films. Figure 2 presents the dependence of magnetization on applied field of two  $V(TCNE)_2$  films. In Figure 2A, the rates are 20:10 (mg/hr TCNE :  $V(CO)_6$ ), while in Figure 2B the rates are 20:2. It can be seen that as the film is richer in V, the coercive field becomes larger, and initial slope of magnetization is shallower. The ratio of initial slope (at lower field) to the slope at higher field is  $\sim 6$  for this film as compared to  $\sim 14$  for the 20:2 ratio film.

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**Figure 2.** Magnetization vs. Field at 5K of  $V(TCNE)_2$  films made under different TCNE :  $V(CO)_6$  sublimation ratios: A) 20:10 (mg/hr), B) 20:2 (mg/hr).

$Co(TCNE)_2$  films, formed also by CVD, are paramagnetic at room temperature. Figure 3 shows the dependence of magnetization on temperature (Figure 3A), and applied field (Figure 3B). Below approximately 100K, the magnetic moment rapidly decreases upon cooling, suggesting antiferromagnetic coupling. This type of behavior has been observed also for powder samples of  $Co(TCNE)_2 \cdot 0.4(CH_2Cl_2)$ , made from  $Co_2CO_8$ . [5]



**Figure 3.** Magnetization vs. Field (Figure 3A), and vs. temperature (Figure 3B) of a  $\sim 500\text{nm}$   $Co(TCNE)_2$  film.

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The electrical and magnetic properties of V(TCNE)<sub>2</sub> thin films were studied. Figure 4A shows the resistance dependence of a ~ 500nm thick V(TCNE)<sub>2</sub> film prepared from a ratio of 20:2 (mg/hr) on temperature. For the high temperature region, the resistance R was found to follow Arrhenius type dependence

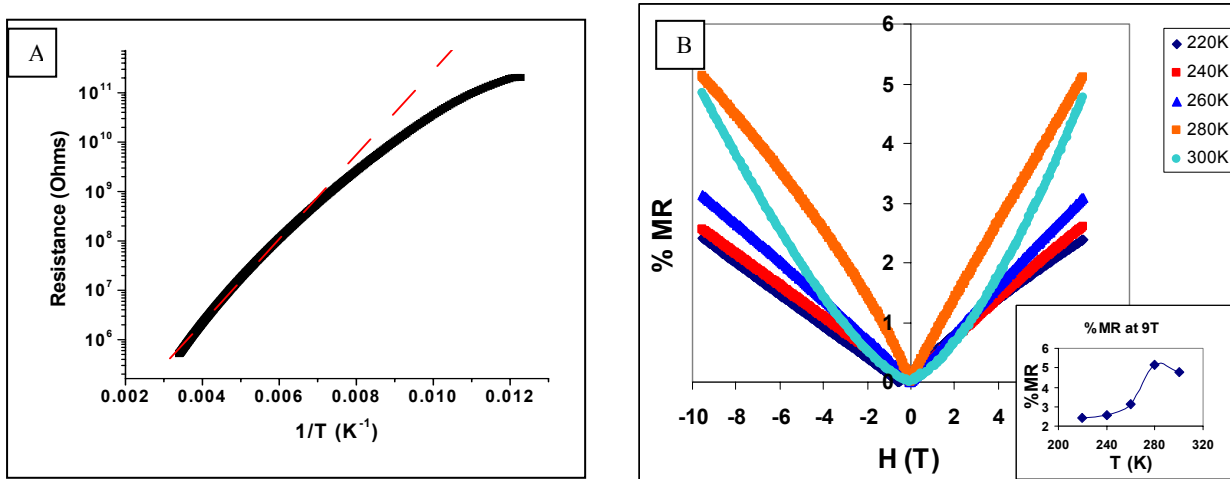
$$R \propto r = A e^{E_a/2k_B T} \quad (3)$$

At lower temperatures, the conduction depends more weakly on temperature, suggesting the role of a hopping mechanism, involving energy states within the gap.[6] The slope of lnR vs. 1/T continuously decreases with temperature. The calculated room temperature activation energy (slope of Figure 4A at 300K) for electron transfer from the valence to the conduction band is ~0.45 eV, in accordance to the value measured for thicker films of 1-5μm.

Figure 4B shows the magnetoresistance as a function of applied magnetic field (parallel to the sample) for various temperature settings. Magnetoresistance is defined as:

$$MR = [\rho(H, T) - \rho(0, T)] / \rho(0, T) \quad (4)$$

There is linear dependence of magnetoresistance on applied field for all temperature plots (except for the 300K). The inset of Fig. 3B describes the magnetoresistance response for all temperatures at 9T. As the temperature of the sample is decreased, the resistance of sample increases. Earlier studies [2,6] of magnetoresistance as a function of applied magnetic field and varying temperature for thick films showed that MR is maximum in the vicinity of the magnetic ordering temperature, T<sub>c</sub>, and that MR is quadratic in applied magnetic field above T<sub>c</sub> in contrast to linear in applied magnetic field below T<sub>c</sub>. The maximum in MR for this thin film at 280K together with the stronger magnetic field dependence at 300K supports that the T<sub>c</sub> for this sample is ~ 280 K. It was earlier shown that T<sub>c</sub> is correlated with magnetic and structural disorder of powder and thick film samples. The linear and quadratic dependencies of the MR on the applied magnetic field can be explained on the basis the conduction gap being a Coulomb gap as we described in *Adv. Mater.* **14**, 1230 (2002). *Adv. Mater.* **14**, 1230 (2002)..



**Figure 4.** A) 500nm V(TCNE)<sub>2</sub> film - Resistance (logarithmic scale) dependence on inverse temperature, B) Magnetoresistance plots as a function of applied field for various temperatures. The inset shows %MR variation with temperature at H=9T.

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Hybrid organic/inorganic spin valve structures were formed, incorporating CVD V(TCNE)<sub>2</sub> films as one of the ferromagnets, and  $\alpha$ -6T as a spacer layer to the other ferromagnet (Co). The choice of an organic spacer layer (in this case a backbone of thiophene units) is motivated by the extremely weak spin-orbit interaction and weak hyper- fine interaction, so that electron spin diffusion length is especially long. The V(TCNE)<sub>2</sub> may offer advantage over conventional metal ferromagnets since its charge transport is proposed to be 100% spin polarized [2]. Using this structure, we expect less spin scattering as the carriers cross interfaces. Spin valve switching was reported for these structures.[7]

The effect of illumination on the magnetic behavior of a  $\sim 1\mu\text{m}$  thick V(TCNE)<sub>2</sub> film was also studied. A photoinduced magnetism was observed using the same spectral region for excitation (the  $\pi \rightarrow \pi^*$  transition band in the ion radical TCNE<sup>•+</sup>) as in the analogous system of Mn(TCNE)<sub>2</sub>·x(CH<sub>2</sub>Cl<sub>2</sub>). This phenomenon may be related to light induced disorder in the sample.

During this project we established the suitability of the organic-based magnetic semiconductor V[TCNE]<sub>2</sub> (TCNE = tetracyanoethanide) as a source of spin polarized electrons with appropriate interface properties for spintronics devices. We have carried out extensive temperature-dependent electron spin resonance studies. These data show ferromagnetic resonance signatures including resonance field that shifts with orientation of the film in the applied magnetic field. The line shapes and the difference in parallel and perpendicular resonance field orientation reflect the domain formation and demagnetization fields. The ESR combined with static and dynamic magnetic susceptibility and magnetization measurements show that the ordering temperature ( $T_c$ ) can be varied from  $>350$  K to less than 200 K. Magnetoresistance (MR) studies show an anomalous behavior with large MR ( $\sim 0.7\%$  at 0.7 T) close to  $T_c$ . The MR is linear in magnetic field below  $T_c$  and quadratic in magnetic field above  $T_c$ . This behavior differs from predictions of conventional models. We have developed a new model based on the TCNE<sup>•-</sup> spins being antiferromagnetically coupled to the V<sup>II</sup> spin 3/2 and the TCNE spins being ferromagnetically ordered among themselves. This leads to split nearly filled and empty Hubbard bands of opposite spin polarization as the source of spin polarized carriers for injection. Initial synchrotron studies of NEXAFS in collaboration with Argonne National Laboratory gave insight into the local structure in these low temperature CVD made films.

We made excellent progress simultaneously in different directions. The organic-based magnet V[TCNE]<sub>2</sub> (TCNE = tetracyano- ethylene), a magnetic semiconductor with  $T_c > 380$  K and a small coercive field ( $<1$  Oe) at room temperature, is of potential interest for a spintronic applications. The coercivity can be enhanced via incorporation of ions with large magnetocrystalline anisotropy (Co, Fe, etc.). Solid solutions of V<sub>x</sub>M<sub>1-x</sub>[TCNE]<sub>2</sub> (M= Co, Fe, Ni) have been synthesized by direct oxidation of TCNE by stoichiometric mixture of vanadium and cobalt, iron or nickel carbonyls in dichloromethane solution. For Co and Fe substantially higher coercive fields,  $H_c$ , than the pure V[TCNE]<sub>2</sub> (275 Oe for  $x = 0.3$  and 1100 Oe for  $x = 0.05$  at 5 K, respectively) were realized, while in case of Ni  $H_c$  does not exceed 14 Oe. The ordering temperature,  $T_c$ , for the materials with  $x > 0.3$  exceeds 300 K. A weak dependence of  $T_c$  for  $x > 0.3$  is consistent with the structural data suggesting a percolation limit of  $< 0.25$ . Despite the ferrimagnetic ordering of V<sub>x</sub>M<sub>1-x</sub>[TCNE]<sub>2</sub> solid solutions, they exhibit spin-glass like behavior at low temperatures in accord with a high structural disorder. The re-entrant behavior is characteristic for many different systems

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especially among the amorphous metallic magnets and is usually related to a drastic increase of the random anisotropy with doping.

MR behavior of  $V[TCNE]_2$  films were measured at National High Magnet Field Lab up to 32 T. Below the ordering temperature films show remarkable linear behavior up to the highest field measured. Above  $T_c$  MR shows a quadratic behavior as expected. Also FMR studies of these films were extended to high frequency to enhance the spectral resolution. Effective magnetization,  $M_{eff}$ , of the sample at different temperatures was obtained from the angular dependence of the resonance field,  $H_r$ . The temperature dependence of the FMR spectra was measured in parallel and perpendicular configurations, and analyzed the resolved peaks. The intensity and linewidth behaviors of individual peaks indicate long-range magnetic ordering and also the presence of glassy nature. These preliminary results could be understood in terms of the formation of multi-domains in the  $V(TCNE)_2$  films.

X-ray absorption spectroscopy was used to determine the chemical oxidation state and local coordination environment of V in  $[TCNE]_2$  molecule-based magnet. The oxidation state of about 2+ obtained by this bulk-sensitive technique is consistent with previous surface sensitive measurements using x-ray photoelectron spectroscopy. Although a mixed valence state for vanadium cannot be ruled out, lack of intrinsic broadening in the leading absorption edge and radial distribution function of V-N distances suggest a single V oxidation state. V ions are coordinated by six N ions, most likely in a slightly distorted octahedral environment. The strong binding between V and TCNE and a 3-D network structure are responsible for the insolubility of this magnet in organic solvents. This local coordination seems to facilitate the remarkable strong magnetic interactions present in this family of molecule-based magnets.

### **III. Listing of all publications and Technical Reports Supported under this Grant**

#### **(a) Papers published in peer-reviewed journals**

1. A.J. Epstein, F.-C. Hsu, N.-R. Chiou, and V.N. Prigodin, *Electric-Field Induced Ion-Leveraged Metal-Insulator Transition in Conducting Polymer-Based Field Effect Devices*, **Current Applied Physics** **2**, 339-343 (2002).
2. V.N. Prigodin, N.P. Raju, K.I. Pokhodnya, J.S. Miller, and A.J. Epstein, *Spin-driven Resistance in Organic-Based Magnetic Semiconductor  $V[TCNE]_x$* , **Advanced Materials** **14**, 1230-1233 (2002).
3. N.P. Raju, T. Savrin, V.N. Prigodin, K.I. Pokhodnya, J.S. Miller, and A.J. Epstein, *Anomalous Magnetoresistance in High-Temperature Organic-Based Magnetic Semiconductor  $V(TCNE)_x$  Films*, **Journal of Applied Physics** **90**, 6799-6801 (2003).
4. V.N. Prigodin, N.P. Raju, K.I. Pokhodnya, J.S. Miller, and A.J. Epstein, *Electronic Spin-Driven Resistance in Organic-Based Magnetic Semiconductor  $V[TCNE]_x$* , **Synthetic Metals** **135-136**, 87-89 (2003).



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5. V.N. Prigodin and A.J. Epstein, *Quantum Hopping in Metallic Polymers*, **Physica B: Physics of Condensed Matter** **338**, 310-317, (2003).
6. K.I. Pokhodnya, V. Burtman, A.J. Epstein, J.W. Raebiger, and J.S. Miller, *Control of Coercivity in Organic-based Solid Solution  $V_xCo_{1-x}[TCNE]_2 \bullet zCH_2Cl_2$  Room Temperature Magnets*, **Advanced Materials** **14**, 1211-1214 (2003).
7. A.J. Epstein, *Organic-based Magnets: Opportunities in Photoinduced Magnetism, Spintronics, Fractal Magnetism, and Beyond*, **Materials Research Society Bulletin** **28**, 492-499 (2003).
8. K.I. Pokhodnya, E.B. Vickers, M. Bonner, A.J. Epstein, and J.S. Miller, *Solid Solution  $V_xFe_{1-x}[TCNE]_2 \bullet zCH_2Cl_2$  Room Temperature Magnet*, **Chemistry of Materials** **16**, 3218-3223 (2004).
9. D. Haskel, Z. Islam, J. Lang, C. Kmety, G. Srajer, K. I. Pokhodnya, A.J. Epstein, and J. S. Miller, *Local Structural Order in the Disordered Vanadium Tetracyanoethylene Room Temperature Molecule-based Magnet*, **Physical Review B** **70**, 054422/1-9 (2004).
10. R. Plachy, K.I. Pokhodnya, P.C. Taylor, J. Shi, J.S. Miller, and A.J. Epstein, *Ferrimagnetic Resonance in Films of Vanadium [Tetracyanoethanide] $_x$ , Grown by Chemical Vapor Deposition*, **Physical Review B** **70**, 064411/1-12 (2004).

(b) Papers published in non-peer-reviewed journals

None

(c) Papers presented at meetings, but not published in conference proceedings

1. V.N. Prigodin and A.J. Epstein, *Origin of Anomalous Magnetoresistivity in Organic-Based Magnetic Semiconductor  $V[TCNE]_x$* , **Meeting of the American Physical Society**, Indianapolis, Indiana, March 18-22, 2002 [Bulletin of the American Physical Society **47**, 66-67 (2002)].
2. Y. Batayev, N.P. Raju, V.N. Prigodin, P. Kahol, R. Plachy, P.C. Taylor, K.I. Pokhodnya, J.S. Miller, and A.J. Epstein, *FMR Studies of High-Temperature Organic-Based Magnetic Semiconductor  $V(TCNE)_x$* , **Meeting of the American Physical Society**, Indianapolis, Indiana, March 18-22, 2002 [Bulletin of the American Physical Society **47**, 722 (2002)].
3. N.P. Raju, T. Savrin, V.N. Prigodin, K.I. Pokhodnya, J.S. Miller, and A.J. Epstein, *Anomalous Magnetoresistance in High-Temperature Organic-Based Magnetic Semiconductor  $V(TCNE)_x$  Films*, **Meeting of the American Physical Society**, Indianapolis, Indiana, March 18-22, 2002 [Bulletin of the American Physical Society **47**, 722 (2002)].

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4. Y. Bataiev, N.P. Raju, T. Savrin, V.N. Prigodin, K.I. Pokhodnya, J.S. Miller, and A.J. Epstein, *Ferrimagnetic Resonance Of High  $T_C$  Organic-Based Magnet  $V(TCNE)_x$  Films*, **Meeting of the American Physical Society**, Austin, Texas, March 3-7, 2003 [Bulletin of the American Physical Society 48, 1252 (2003)].
5. N.P. Raju, V.N. Prigodin, K.I. Pokhodnya, J.S. Miller, and A.J. Epstein, *High Field Positive Magnetoresistance In Organic-Based Magnetic Semiconductor  $V(TCNE)_x$  Films*, **Meeting of the American Physical Society**, Austin, Texas, March 3-7, 2003 [Bulletin of the American Physical Society 48, 1252 (2003)].
6. K.I. Pokhodnya, V. Burtman, J. Raebiger, A.J. Epstein, and J.S. Miller *Re-entrant Behavior of Ferrimagnetic  $V_xCo_{1-x}[TCNE]_2$  Organic-based Magnets*, **Meeting of the American Physical Society**, Austin, Texas, March 3-7, 2003 [Bulletin of the American Physical Society, <http://www.aps.org/meet/MAR03/baps/abs/S8640.html#SX24.015> X24.015 (2003)].
7. Y. Bataiev, N.P. Raju, K.I. Pokhodnya, A.J. Epstein, and J.S. Miller, *Ferrimagnetic Resonance of  $V_xCo_{1-x}[TCNE]_2$  Organic-Based Magnetic Semiconductors*, **Meeting of the American Physical Society**, Montreal, Canada, March 22-26, 2004 [Bulletin of the American Physical Society 49, 486 (2004)].
8. K.I. Pokhodnya, A.J. Epstein, and J.S. Miller, *Transport Properties of Molecule-Based  $V[TCNE]_x$  Magnetic Films*, **Meeting of the American Physical Society**, Montreal, Canada, March 22-26, 2004 [Bulletin of the American Physical Society 49, 486 (2004)].

(d) Manuscripts submitted but not published

None

(e) Technical reports submitted to ARO

None

(f) Presentations citing ARO Support:

f.1. Invited Talks at National and International Meetings:

1. V.N. Prigodin, N.P. Raju, A.J. Epstein, K.I. Pokhodnya, and J.S. Miller, *Spin-Driven Magnetoresistance in Molecule Magnetic Semiconductor  $V[TCNE]_x$* , **International Conference on Science and Technology of Synthetic Metals**, Shanghai, P.R. China, June 29-July 5, 2002.
2. V.N. Prigodin and A.J. Epstein, *Quantum Hopping in Metallic Polymers*, **6<sup>th</sup> International Conference on the Electrical Transport and Optical Properties of Inhomogeneous Media**, Snowbird, Utah, July 15-19, 2002.

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3. A.J. Epstein, *Electronics and Magnetism From Polymer/Molecular Materials: Recent Advances and New Opportunities*, **Center for Molecular Science Forum**, Institute of Chemistry, Chinese Academy of Sciences, Beijing, PRC, July 16, 2002.
4. A.J. Epstein, *Magnetism and Electronics From Polymer/Molecular Materials: Recent Advances and New Opportunities*, **Ceremonies for Installation as Honorary Professor**, Jilin University and Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun, PRC, July 19, 2002.
5. A.J. Epstein, N.P. Raju, K.I. Pokhodnya, J.S. Miller, and V.N. Prigodin, *Spin-Driven Resistance in Organic-Based Magnetic Semiconductor  $V[TCNE]_x$* , **VIIIth International Conference on Molecule-based Magnets**, Valencia, Spain, October 5-10, 2002.
6. N.P. Raju, V.N. Prigodin, K.I. Pokhodnya, and A.J. Epstein, *Spin-Driven Resistance in Organic-Based Magnetic Semiconductor  $V[TCNE]_x$  ( $x \sim 2$ )*, **Materials Research Society 2002 Fall Meeting**, Boston, Massachusetts, December 2-6, 2002.
7. A.J. Epstein, *Introduction to Organic Based Magnets, From Low and High Temperature Magnets to Materials for Photo-Induced Magnetism and Spintronics*, **Materials Research Society 2002 Fall Meeting**, Boston, Massachusetts, December 2-6, 2002.
8. A.J. Epstein, *Organic-based Magnets: New Concepts for Science and Technology*, **New Mountains to Climb: New Phenomena, Materials and Technologies for the 21<sup>st</sup> Century, Festschriften Honoring Alan G. MacDiarmid's Achievements for his 75<sup>th</sup> Year**, Dallas, Texas, December 6-7, 2002.
9. A.J. Epstein, *Magnetism, Spin, and Organic Molecules*, **NSF Workshop Technological Challenges For Flexible, Light-Weight, Low-Cost and Scalable Organics, Electronics and Photonics**, Arlington, Virginia, January 16-17, 2003.
10. A.J. Epstein, *Magnetism from Organic Molecules: From Alchemy to Potential Applications*, **AMN-1: An International Conference on Advanced Materials and Nanotechnology**, Wellington, New Zealand, February 9-14, 2003.
11. A.J. Epstein, *Photoinduced Magnetism in Organic-Based Magnets*, **Fifth International Topical Conference on Optical Probes of Conjugated Polymers and Organic and Inorganic Nanostructures**, Venice, Italy, February 9-14, 2003.
12. A.J. Epstein, *New Physics and Phenomena: From Photoinduced Magnetism to Spintronic Materials*, **Meeting of the American Physical Society**, Austin, Texas, March 3-7, 2003.
13. A.J. Epstein, *Room Temperature Organic-based Magnetic Semiconductor  $V[TCNE]_2$* , **Organic/Polymeric Spintronics Workshop**, Baltimore, MD, April 14-15, 2003.

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14. A.J. Epstein, *Room Temperature Organic-based Magnetic Semiconductor  $V[TCNE]_2$  – Opportunities for Spintronic Applications*, **Workshop on Fundamental Research Needs in Organic Electronic Materials**, Salt Lake City, UT, May 23-25, 2003.
15. A.J. Epstein, *New Developments in Magnetism from Organic Based Magnets*, **Alvin L. Kwiram Symposium on Optical, Electrical, and Magnetic Properties of Organic and Hybrid Materials**, Seattle, WA, June 23-25, 2003.
16. A.J. Epstein, *Conventional and Unconventional Magnetism in Organic-Based Solids: New Opportunities in New Materials*, **The 2003 Ralph and Helen Oesper Symposium**, University of Cincinnati, October 11, 2003.
17. J.S. Miller, *Organic Magnets: New Chemistry, New Bonding, and New Materials for the New Millennium*, **The 2003 Ralph and Helen Oesper Symposium**, University of Cincinnati, October 11, 2003.
18. A.J. Epstein, *Organic-Based Magnets: From Discovery to Room Temperature Magnets, Photoinduced Magnetism and Spintronics*, **Colloquium, Industrial Technology Research Institute**, Hsinchu, Taiwan, November 4, 2003.
19. A.J. Epstein, *Organic-based Magnets Fractal Behavior, Photoinduced Magnetism, and Spintronics*, **International Conference on Quantum Transport in Synthetic Metals and Quantum Functional Semiconductors**, Seoul, Korea, November 20-22, 2003.
20. A.J. Epstein and J.S. Miller, *Conventional and Unconventional Magnetism in Organic-Based Solids: New Opportunities in New Materials*, **9<sup>th</sup> Joint MMM/Intermag Conference**, Anaheim, California, January 5-9, 2004.
21. A.J. Epstein, *Spintronics: What is it? Why use Organics/Polymers?*, **Center for Materials Research Faculty Seminar, The Ohio State University**, Columbus, Ohio April 26, 2004.
22. A.J. Epstein, *Electronic/Magnetic/Photonic Polymers*, **Ohio State University Polymer Consortium Review**, Columbus, Ohio, April 27, 2004.
23. A.J. Epstein, Key Note Address, *Organic-Based Magnets: New Materials, New Phenomena, and New Applications*, **226<sup>th</sup> Fragrant Hills Symposium On Molecular and Plastic Electronics and Opto-Electronics (Xiangshan Science Conference)**, Beijing, May 20-22, 2004.
24. A.J. Epstein, *Organic- and Polymer- Based Magnets: New Materials, New Phenomena, and New Applications*, **Conference for the Celebration of 50 Years of Polymer Science at Peking University**, Beijing, P.R. China, May 28, 2004.

f.2. Contributed Talks at National and International Meetings:

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1. Y. Batayev, N.P. Raju, V.N. Prigodin, P. Kahol, R. Plachy, P.C. Taylor, K.I. Pokhodnya, J.S. Miller, and A.J. Epstein, *FMR Studies of High-Temperature Organic-Based Magnetic Semiconductor  $V(\text{TCNE})_x$* , **Meeting of the American Physical Society**, Indianapolis, Indiana, March 18-22, 2002 [Bulletin of the American Physical Society 47, 722 (2002)].
2. N.P. Raju, T. Savrin, V.N. Prigodin, K.I. Pokhodnya, J.S. Miller, and A.J. Epstein, *Anomalous Magnetoresistance in High-Temperature Organic-Based Magnetic Semiconductor  $V(\text{TCNE})_x$  Films*, **Meeting of the American Physical Society**, Indianapolis, Indiana, March 18-22, 2002 [Bulletin of the American Physical Society 47, 722 (2002)].
3. V.N. Prigodin and A.J. Epstein, *Origin of Anomalous Magnetoresistivity in Organic-Based Magnetic Semiconductor  $V[\text{TCNE}]_x$* , **Meeting of the American Physical Society**, Indianapolis, Indiana, March 18-22, 2002 [Bulletin of the American Physical Society 47, 66-67 (2002)].
4. S.J. Etzkorn, W. Hibbs, J.S. Miller, and A.J. Epstein, *Viscous Behavior in an Organic-Based Quasi-1D Fractal Cluster Glass*, **VIIIth International Conference on Molecule-based Magnets**, Valencia, Spain, October 5-10, 2002.
5. D.A. Pejakovic, C. Kitamura, J.S. Miller, and A.J. Epstein, *Photoinduced Magnetism and Metastability in Organic-Based Magnet  $\text{Mn}(\text{TCNE})_2 \cdot x(\text{CH}_2\text{Cl}_2)$* , **VIIIth International Conference on Molecule-based Magnets**, Valencia, Spain, October 5-10, 2002.
6. Y. Bataiev, N.P. Raju, T. Savrin, V.N. Prigodin, K.I. Pokhodnya, J.S. Miller, and A.J. Epstein, *Ferrimagnetic Resonance of High  $T_c$  Organic-Based Magnet  $V[\text{TCNE}]_x$  Films*, **Meeting of the American Physical Society**, Austin, Texas, March 3-7, 2003 [Bulletin of the American Physical Society 48, 1252 (2003)].
7. N.P. Raju, V.N. Prigodin, K.I. Pokhodnya, J.S. Miller, and A.J. Epstein, *High Field Positive Magnetoresistance in Organic-Based Magnetic Semiconductor  $V(\text{TCNE})_x$  films*, **Meeting of the American Physical Society**, Austin, Texas, March 3-7, 2003 [Bulletin of the American Physical Society 48, 1252 (2003)].
8. K.I. Pokhodnya, V. Burtman, J. Raebiger, A.J. Epstein, and J.S. Miller *Re-Entrant Behavior of Ferrimagnetic  $V_x\text{Co}_{1-x}[\text{TCNE}]_2$  Organic-Based Magnets*, **Meeting of the American Physical Society**, Austin, Texas, March 3-7, 2003.
9. V.N. Prigodin and A.J. Epstein, *Screening of Electric Field in a Variable Range Hopping System*, **Meeting of the American Physical Society**, Austin, Texas, March 3-7, 2003 [Bulletin of the American Physical Society 48, 81 (2003)].
10. Y. Bataiev, N.P. Raju, K.I. Pokhodnya, A.J. Epstein, and J.S. Miller, *Ferrimagnetic Resonance of  $V_x\text{Co}_{1-x}[\text{TCNE}]_2$  Organic-Based Magnetic Semiconductors*, **Meeting of the**

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**American Physical Society**, Montreal, Canada, March 22-26, 2004 [Bulletin of the American Physical Society 49, 486 (2004)].

11. K.I. Pokhodnya, A.J. Epstein, and J.S. Miller, *Transport Properties of Molecule-Based V[TCNE]<sub>x</sub> Magnetic Films*, **Meeting of the American Physical Society**, Montreal, Canada, March 22-26, 2004 [Bulletin of the American Physical Society 49, 486 (2004)].

f.2. Seminars and Colloquia:

1. A.J. Epstein, *Organic-Based Magnets*, **Watkins Visiting Professor Seminar, Department of Physics, Wichita State University**, Wichita, Kansas, March 5, 2002.
2. A.J. Epstein, *Organic-based Magnets, From an Unknown to Photoinduced Magnetism and Spintronics*, **Colloquium, University of Buffalo at SUNY**, Buffalo, New York, April 25, 2002.
3. A.J. Epstein, *Organic-based Magnets: From Impossibility to Fractal Magnets, Photoinduced Magnetism and Spintronics*, **Colloquium**, The Ohio State University, Columbus, Ohio, January 7, 2003.
4. A.J. Epstein, *Organic-Based Magnets: From Low and High Temperature Magnets to Photoinduced Magnetism and Spintronics*, **Colloquium, Joint Institute of Chemical Physics**, Moscow, Russia, September 5, 2003.
5. A.J. Epstein, *Organic-Based Magnets: From Discovery to Room Temperature Magnets, Photoinduced Magnetism and Spintronics*, **Colloquium, Ioffe Institute**, Saint Petersburg, Russia, September 9, 2003.
6. A.J. Epstein, *Organic-Based Magnets*, **Society for Physics Students Seminar, Physics Department, The Ohio State University**, Columbus, Ohio, February 10, 2004.
7. A.J. Epstein, *Organic-Based Magnets: New Materials, New Phenomena, and New Applications*, **Colloquium, Physics Department, Case Western Reserve University**, Cleveland, Ohio, April 22, 2004.
8. A.J. Epstein, *Organic-Based Magnets: New Materials, New Phenomena, and New Applications*, **Colloquium, Institute of Applied Chemistry, Chinese Academy of Sciences**, Changchun, P.R. China, May 17, 2004.
9. D. Haskel, Z. Islam, J. Lang, C. Kmety, G. Srajer, K. I. Pokhodnya, A.J. Epstein, and J. S. Miller, *Local Structural Order in the Disordered Vanadium Tetracyanoethylene Room Temperature Molecule-based Magnet*, **Physical Review B** 70, 054422/1-9 (2004).

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**IV. List of all participating scientific personnel showing any advanced degrees earned by them while employed on the project.**

1. Dr. Arthur J. Epstein, Distinguished University Professor (Principal Investigator)
2. Dr. Raju Nandyala, Research Associate
3. Dr. Vladimir Burtman, Postdoctoral Researcher
4. Dr. Kostyantyn Pokhodnya, Visiting Scientist
5. Dr. Stephen Etzkorn, Graduate Student/Postdoctoral Researcher  
S. Etzkorn received his Ph.D. in Physics while employed on this project.

**V. Report of inventions (by title only)**

Spin Driven Resistors and Nanogates: U.S. Patent 7,075,815

**VI. Bibliography**

N/A

**VII. Appendixes**

None